Jet Fuel Thermal Stability Investigations using Ellipsometry

Leigh Nash[1] and Subith S. Vasu[2]
Center for Advanced Turbomachinery and Energy Research (CATER), University of Central Florida, Orlando, Florida, 32816

and

Jennifer Klettlinger[3]
NASA Glenn Research Center, Cleveland, Ohio, 44135

Jet fuels are typically used for endothermic cooling in practical engines where their thermal stability is very important. In this work the thermal stability of Sasol IPK (a synthetic jet fuel) with varying levels of naphthalene has been studied on stainless steel substrates using spectroscopic ellipsometry in the temperature range 385-400 K. Ellipsometry is an optical technique that measures the changes in a light beam's polarization and intensity after it reflects off of a thin film to determine the film's thickness and optical properties. All of the tubes used were rated as thermally unstable by the color standard portion of the Jet Fuel Thermal Oxidation Test, and this was confirmed by the deposit thicknesses observed using ellipsometry. A new amorphous model on a stainless steel substrate was used to model the data and obtain the results. It was observed that, as would be expected, increasing the temperature of the tube increased the overall deposit amount for a constant concentration of naphthalene. The repeatability of these measurements was assessed using multiple trials of the same fuel at 385 K. Lastly, the effect of increasing the naphthalene concentration in the fuel at a constant temperature was found to increase the deposit thickness.

Nomenclature

JFTOT	=	Jet Fuel Thermal Oxidation Test
k	=	extinction coefficient
f_j	=	oscillator strength
n	=	index of refraction
Γ_j	=	broadening factor
ω_p	=	frequency corresponding to zero ε_r
ω_j	=	energy of the maximum extinction coefficient
ω_g	=	energy band gap

I. Introduction

Jet fuel thermal stability is a topic of intense research because of its importance in fuel cooled advanced aero engines [1-3]. Alternative jet fuels are of interest in the aviation community because of rising oil costs, the need to secure a consistent supply, and the possibilities for cleaner burning engines [4]. Before alternative fuels are certified for use in flight they are rigorously tested and qualified. An important jet fuel property that must be characterized is the thermal stability, which is a measure of the degree to which a fuel starts to break down when it is heated. As a weight and space saving measure, the fuel in an aircraft is also generally used as engine coolant. This preheating of the fuel before it is burned can cause it to start to breakdown inside the engine pluming (known as coking[5]), fouling the lines and leading to a loss of fuel flow. It is important to know the way a fuel will thermally decompose and the amount of deposit that is formed in order to anticipate maintenance schedules and possible fuel flow issues.

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[1] Graudate Researcher, Center for Advanced Turbomachinery and Energy Research, Mechanical and Aerospace Engineering, University of Central Florida, Orlando, FL 32816, AIAA Student Member
[2] Assistant Professor, Center for Advanced Turbomachinery and Energy Research, Mechanical and Aerospace Engineering, University of Central Florida, Orlando, FL 32816, AIAA Member
[3] Research Chemical Engineer, NASA Glenn Research Center, Cleveland, Ohio, 44135, AIAA Member

In the past, the Jet Fuel Thermal Oxidation Test (JFTOT) relied solely on a comparison between a color standard and the deposits left on a heated tube after the fuel was flowed over it to determine thermal stability (this method is still used to produce the tubes analyzed by ellipsometry and is detailed in the Experiment section). A fuel was rated as thermally stable at a particular temperature if it rated a 3 or less on the color scale [6], see Figure 1. These comparisons were deemed to be non-objective and non-repeatable, which lead to the implementation of ellipsometry to measure film deposit thicknesses [7]. The ellipsometry thermal stability criteria is that the thickest part of the deposit be less than 85 nm in thickness. Ellipsometry is a useful technique for this type of application because it is nondestructive and a relatively simple procedure to perform. It is also very sensitive to minor changes in the deposit thickness, making it very precise. It is also important to note that the color standard method was only applicable to conventional fuels on aluminum substrates because of the differences in deposit color that can occur with different substrates and alternative fuels. This work focuses on stainless steel substrates because of their applicability to aviation engines.

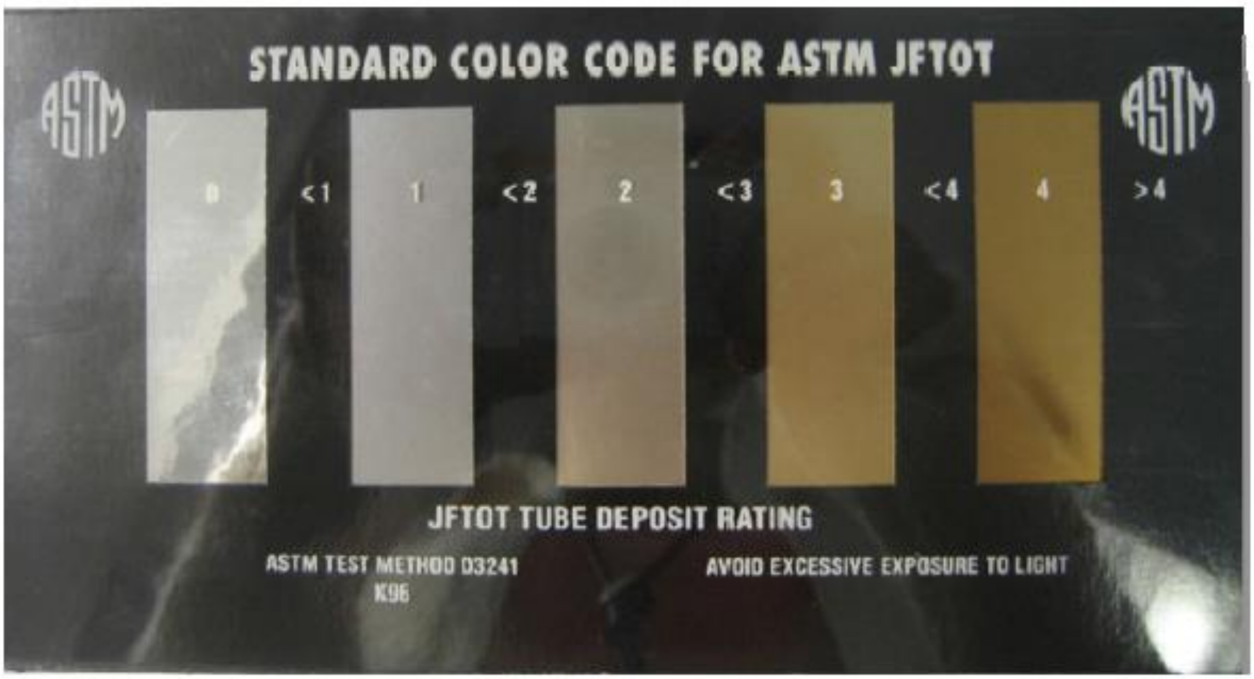

Figure 1. JFTOT Color Standard [7]

Sasol IPK (iso-paraffinic kerosene) is a Fisher-Tropsch synthetic jet fuel. This alternative fuel is mostly composed of C_{10} and C_{12} iso-paraffns [8], and it contains far fewer components than traditional fuels which can have hundreds of components. A typical IPK fuel produced by Sasol contains 2.6 percent cycloparafinns, and 97.4 n- and iso-paraffins as show in [9]. The additive tested in this work is naphthalene, a 2 ringed aromatic structure.

Ellipsometry is a much preferable method as opposed to the JFTOT because it produces a numerical result which can be objectively analyzed. If a fuel produces 85 nm or less of deposit at a particular temperature, the fuel is rated as thermally stable at that temperature. Other advantages of ellipsometry are that it is sensitive to angstrom level thickness, as well as composition changes.

II. Methods

Ellipsometry is an optical technique that uses changes in light polarization to measure the properties of a thin film. The film's thickness, composition, and structure, among other properties, can be determined using ellipsometry. This study is concerned with the thickness. When light crosses an interface, the phase and intensity of the wave changes. The light reflects and refracts at the contact plane between the two materials, and in a multi-layer material, this occurs at each interface (see Figure 2). This means that the overall reflected beam is made up of components from each interfacial interaction. . These components interact with each other, producing interference in the overall beam. The overall beam can be analyzed to determine features of the film and its individual layers. The properties of this beam can be traced backwards though each medium change, and in this way, the thickness can be determined using the Fresnel equations, see Equation 1 and 2, where β is the phase change for a beam of light that passes twice through the material.

$$R^p = \frac{r_{12}{}^p + r_{23}{}^p \exp(\text{-}j2\beta)}{1 + r_{12}{}^p r_{23}{}^p \exp(\text{-}j2\beta)}$$

(Equation 1)

$$R^s = \frac{r_{12}{}^s + r_{23}{}^s \exp(\text{-}j2\beta)}{1 + r_{12}{}^s r_{23}{}^s \exp(\text{-}j2\beta)}$$

(Equation 2)

For multi-layer samples, the thickness cannot be determined analytically, so it is done by assuming a thickness for each layer, calculating what the properties of the reflected beam would be, and comparing the results to those obtained experimentally. The guess for the thickness is altered until the theoretical and experimental results match [10]. This numerical fitting procedure is done using Horiba Scientific's software DeltaPsi2 in this study.

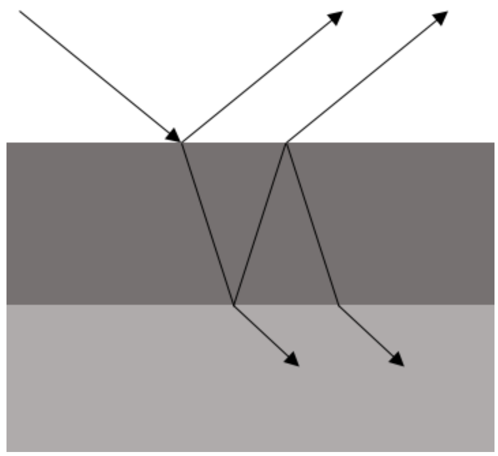

Figure 2. Light behavior at an interface

In the most basic sense, an ellipsometer is made up of a light source, polarizer, detector, and analyzer. After leaving the source, the light is given a linear polarization. The light then encounters the sample. After reflection off of the film, it is elliptically polarized, and it enters the detector. The shape of the ellipse contains the information that yields the film properties after analysis.

A Horiba Scientific spectroscopic ellipsometer (Auto SE) was used to take the data in this study. The Auto SE has a spectral range of 400 to 1100 nm and 70° angle of incidence. The sample viewer is a CCD camera with a field of view of 1.33 by 1 mm and a resolution of 10 µm. A small spot size was used in order to minimize the effect of the tubes' curved surfaces.

The tubes were made using an Alcor Hot Liquid Process Simulator model HLPS-400, following the JFTOT procedure given in ASTM D3241.

A new amorphous dispersion formula was used to model the deposits on the stainless steel tubes. A dispersion formula is used when the optical constants (index of refraction and coefficient of extinction) for a material change with wavelength. The new amorphous dispersion is described by Equations 3 through 7 [11].

$$k(\omega) = \sum_{j=1}^{N} \frac{f_j(\omega\text{-}\omega_g)^2}{(\omega\text{-}\omega_j)^2 + \Gamma_j{}^2} \; for\ \omega > \omega_g$$

(Equation 3)

$$k(\omega) = 0 \; for\ \omega \le \omega_g$$

(Equation 4)

$$n(\omega) = n_\infty + \sum_{j=1}^{N} \frac{B_j(\omega\text{-}\omega_j) + C_j}{(\omega\text{-}\omega_j)^2 + \Gamma_j^{\,2}}$$

(Equation 5)

$$B_j = \frac{f_j}{\Gamma_j}\left[\Gamma_j^{\,2}\text{-}(\omega_j\text{-}\omega_g)^2\right]$$

(Equation 6)

$$C_j = 2 f_j \Gamma_j (\omega_j\text{-}\omega_g)$$

(Equation 7)

A data file taken for a clean stainless steel tube was used for the substrate. This was done to account for any oxidation layer that may be present on the tube surface without having to include a separate oxide layer in the model.

III. Results

Stainless steel tube substrates were analyzed with Sasol IPK over a temperature range of 385 to 400 K with 0 to 5 percent naphthalene by volume. The modeling for these tubes was done using a new amorphous dispersion for a hydrocarbon layer on a stainless steel tube. All but one of these tubes scored a 4 on the JFTOT color scale, and the remaining one scored a 3, meaning that all of them failed the color test for thermal stability. All of them resulted in maximum thicknesses that would also rate them as thermally unstable (>85nm). This is not surprising as all of the tubes showed very dark deposits that were visible to the eye.

Table 1. Results Summary

Tube Number	Temperature (K)	Fuel	Average Chi Squared	Average Deposit Thickness (Å)	Average Clean Thickness (Å)	Thickness P/F	JFTOT Color P/F
1308	390	N118 SASOL IPK (100 %vol)	0.301139897	1089.1	472.318	F	4 F
1309	385	N118 SASOL IPK (100 %vol)	0.278225966	1037.438	456.449	F	3 F
1311	385	N136 SASOL IPK-1-M-Napthalene (99-1 %vol)	0.182131586	1134.873	348.649	F	4 F
1328	400	N139 SASOL IPK-1,2,3,4-T-Napthalene (99-1 %vol)	0.387912966	1530.237	763.326	F	4 F
1329	385	N139 SASOL IPK-1,2,3,4-T-Napthalene (99-1 %vol)	0.219484345	1278.222	511.909	F	4 F
1332	385	N140 SASOL IPK-1,2,3,4-T-Napthalene (97-3 %vol)	0.25248431	1307.806	624.362	F	4 F
1333	385	N141 SASOL IPK-1,2,3,4-T-Napthalene (95-5 %vol)	0.27106469	1796.44	497.263	F	4 F
1339	385	N136 SASOL IPK-1-M-Napthalene (99-1 %vol)	0.13755969	559.838	364.465	F	3 F

A. Effect of Increasing Temperature

It can be seen that there is an overall increasing trend in deposit thickness as the temperature is increased for constant naphthalene concentration as can be seen when comparing tubes 1308 and 1309 for 0 percent naphthalene. The absolute maximum thickness, the average deposit thickness, and the average clean thickness all increase with the increase in temperature. The same increasing trend in deposit thickness with increasing temperature is also seen for 1311 and 1328 for 1 percent naphthalene (see Figures 3 and 4). The absolute maximum thickness, average deposit thickness, and average clean thickness all increase. These increases are greater than for the 0 percent naphthalene tubes, however the range here is also larger. If the increase in thickness is assumed to be linear, then for an equal increase in temperature the average deposit thickness and the average clean thickness for the 1 percent naphthalene increases more.

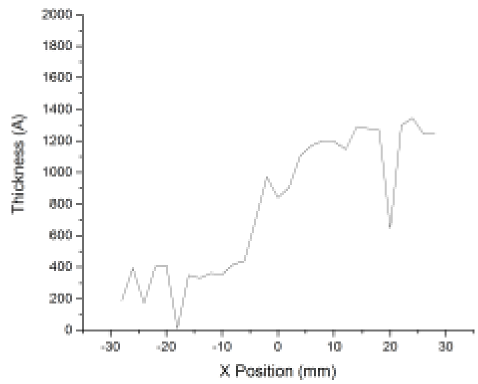

Figure 3. Tube 1311

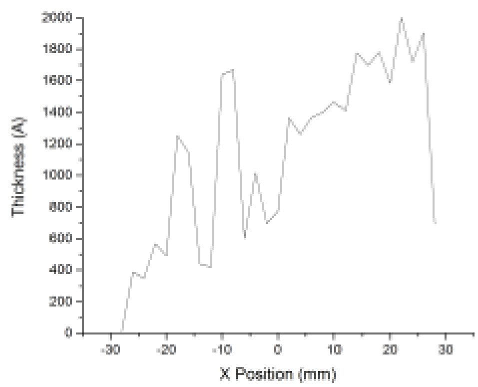

Figure 4. Tube 1328

B. Repeatability

Tubes 1311, 1329, and 1339 are different trials for the same fuel concentrations and temperatures. The average deposit thicknesses of tubes 1311 and 1329 show good similarity. The average clean thicknesses are different, but that can be attributed to differences in the tube surface.

C. Effect of Increasing Naphthalene Concentration

Tubes 1309, 1329, 1332, and 1333 show the effect of increasing naphthalene concentration at a constant temperature. It is seen that increasing the amount of naphthalene here increases the maximum deposit thickness. With increasing naphthalene concentration, the average deposit thickness increases while the average clean thickness stays approximately the same. The fuel used for tube 1309 contains no naphthalene and this tube also show the least amount of deposit, so for the stainless steel cases naphthalene is decreasing the thermal stability of the fuel.

IV. Conclusion

In conclusion, ellipsometry was used to investigate the thermal stability of jet fuels on stainless steel substrate. The effects of increasing temperature and addition of naphthalene on stainless steel tubes with Sasol IPK fuel were investigated. It was found, as expected, that increasing temperature lead to an increase in deposit thickness. It was also found that increasing amounts of naphthalene increased the maximum deposit thickness. The repeatability of these measurements was investigated using multiple tests at the same conditions. The present work provides as a better quantitative tool compared to the widely used JFTOT technique. Future work will expand on the fuel types, temperature, and substrate materials.

Acknowledgments

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